PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Cracking or Coking Heavy Hydrocarbon Oils

We, Esso Research and Engineering Company, formerly known as Standard Oil Development Company, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, or Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for treating heavy hydrocarbons and more particularly relates to the cracking or coking of heavy residual oils to produce lower boiling hydrocarbons and coke.

The hydrocarbon heavy oil which is to be cracked according to the present process is a high boiling hydrocarbon oil which cannot be vaporized at ordinary pressures without cracking the high boiling constituents. It is preferably the residual oil that is produced by distilling crude petroleum oil at ordinary atmospheric pressure or under subatmospheric pressure such as vacuum distillation. The present process may also be used for cracking or coking shale oils, pitches or tars.

Processes are known in the prior art for cracking or coking residual oils in the presence of finely divided inert or substantially inert solids maintained as a liquidized bed.

One of the problems in the fluid coking of heavy oil feeds such as residual oils in the distribution of the heavy residual oil feed on the coke or other hot particles in the fluid bed in the coking zone. In previous work on coking difficulty was experienced when oil was fed in at one side of the reactor. The opposite wall of the reactor has in some instances coked up because of the impingement of oil feed against such opposite wall.

In carrying out the process of the present invention agglomeration of the coke particles at the oil feed injection point is prevented by providing a high velocity mixing zone for the coke particles and injecting the residual oil feed into this high velocity mixing zone in which the motion of the coke or other solids is so turbulent that good distribution of the oil on the particles is obtained, while at the same time it is difficult for the particles to stick together because of their momentum at the high velocity.

The present invention comprises a method of converting into lower-boiling hydrocarbons heavy hydrocarbon oils which consist of constituents which cannot be vaporized without cracking at atmospheric pressures, which comprises introducing preheated heavy hydrocarbon oil into a mixing zone, while passing through said mixing zone solid non-catalytic refractory particles at a turbulent velocity, passing the resultant mixture of oil and solid particles into a dense fluidized bed of similar solid refractory particles maintained at an elevated temperature to produce lower boiling hydrocarbons therein while depositing coke on the said solid particles, removing the coked solid particles from the said reaction zone and passing them to a combustion zone wherein oxygen containing gas is introduced to burn the coke and heat the solid particles to a temperature above that existing in the said reaction zone returning at least part of the heated solid particles from the said combustion zone to the said dense fluidized bed to supply heat thereto.

In one form of the invention the aeration gas such as superheated steam which is to fluidize the lower part of the bed of solids in the coking zone is first used to obtain high solid flow rates through an external circulating leg into which the residual oil feed is introduced at one or more points. This double use of aeration steam for the feed injection section is one important saving. The circulating leg is preferably a **U**-bend which is used to withdraw solids from the fluidized bed and return them through a dense phase riser into which the oil feed is introduced.

Other forms of circulating legs may be used. In addition in some cases hot solids from the burner may be introduced into the rise or upflow leg before the oil feed is introduced.

In another form of the invention, the high velocity zone is created in an internal vertical draft tube, as hereinafter described.

Referring to the accompanying drawings:—

Fig. 1 represents diagrammatically one form of apparatus adapted for carrying out the process of the present invention using an external circulating leg;

Fig. 2 represents an enlarged vertical cross section of the preferred means of introducing oil feed into the circulating leg; and

Fig. 3 diagrammatically represents a modified form of apparatus in which an internal circulating leg is used.

Referring now to Fig. 1 of the drawing, the reference character 10 designates a reactor or coking zone containing a fluidized dense bed 12 of solid finely divided inert particles such as coke. The dense bed 12 has a level indicated at 14 with a dilute phase 16 thereabove. The inert solids of the fluidized bed 12 have a particles size between about 50 and 600 microns, preferably between about 100 and 400 microns and may comprise petroleum coke, or other coke, coke formed in the process, spent cracking catalyst, pumice, alumina or other refractory materials.

The fluidized bed 10 is maintained at a temperature between about 800° and 1600° F. or higher. When coking to produce motor fuel such as gasoline, temperatures in the lower range of about 800° to about 1200° F., preferably about 900° to 1100° F. will be used, whereas, when coking at extremely high temperatures to produce chemicals such as unsaturated hydrocarbon gases and aromatic hydrocarbons, temperatures in the higher range of about 1200° F. to about 1600° F. preferably about 1250° to 1450° F. will be used.

The preheated oil feed is introduced through line 18 into the upflow leg or riser 22 of **U**-bend 24. Riser 22 empties into reactor 10 at the lower conical section 25 thereof. Solids from the dense fluidized bed 12 are withdrawn through downflow leg or standpipe 26. The **U**-bend 24 forms an external solids circulating means whereby a high velocity zone is provided whereinto the residual oil is fed through one or more points. More than one **U**-bend may be used if desired but the number is kept small to provide relatively large diameter legs of the **U**-bend to reduce heat losses and to provide more mixing volume with less attendant pipe wall surface.

Aeration steam which is usually introduced into the fluid bed 12 and which is required to fluidize the lower portion of the dense bed 12 is introduced through line or lines 28 above valve or restricted orifice 30 arranged in riser 22. Orifice 30 provides sufficient pressure drop to control the solids circulation within the desired limits. Instead of using orifice 30 a slide valve (not shown) may be used in downflow leg or standpipe 26 to control the rate of flow of solids through the circulating means. The preferred means of control of flow, however, is to control the amount and point of introduction of steam or gas through line 28, line 54 and other lines (not shown) similarly located along the line 22. Valve 30 is then used only as a positive shut-off valve.

The preferred form of introducing the residual oil feed into riser 22 is shown in an enlarged detail in Fig. 2. The upflow leg or riser 22 is provided intermediate to its ends with a constricted zone or Venturi section 32 at which zone the gas velocity and solids velocity are accelerated. The residual oil is introduced near the point of maximum solids and gas velocity. The point or points of oil feed introduction is preferably a short distance or slightly downstream from the first region of maximum constriction and may be slightly downstream from the "venacontracta" or point of maximum gas velocity at 34.

Oil feed from line 18 is passed to manifold 36 from which the oil is fed through a plurality of nozzles 38, preferably high velocity nozzles. The constricted zone 32 is shown as provided with openings 40 for nozzles 38. By introducing the oil feed at this region of high gas and solids velocity, good distribution of the oil on the solids is obtained due to the turbulent motion of the solids. At the same time the hot particles containing the distributed oil feed do not stick together because of their momentum at the high velocity. The oil feed is well mixed with the hot solids in the riser 22 and the mixture is then introduced continuously into the center of the large dense fluid highly turbulent bed 12 in the reactor 10 as an up-draft stream so that wet solids are kept away from the internal wall of reactor 10 for the maximum length of time and no coking of the oil takes place on the internal wall of the reactor.

By using a relatively long riser line, time is allowed for some cracking to take place in the riser line. This reduces solids holdup in the reactor 10 and at the same time provides more gas in the riser line 22

for aeration of the fluid bed 12 in reactor 10.

If desired, residual oil feed from line 18 may be introduced into riser 22 at more points above and below the constriction 32 as shown at lines 42 and 44. Injection lines may extend into the solids stream in riser 22, pointing upward so as to keep the high velocity feed jet from impinging on the walls of riser 22. An internal nozzle of this type should be insulated on the outside to keep the metal at feed temperature and thus prevent coking. Constrictions similar to that shown at 32 may be used in riser 22 at these points of feed injection.

Instead of introducing residual oil feed through line 42, a more refractory oil feed such as cycle oil or condensate oil separated from the products of coking may be introduced through line 46 and line 42 to crack the more refractory oil stock at a higher temperature and also hold it at a cracking temperature for a longer period of time. The temperature of the hot solids in **U**-bend 24 may be increased by introducing hot solids such as coke particles from burner or combustion zone 48, later to be described in greater detail, through line 49 and line 50 into riser 22 above valve or orifice 30. Additional hot coke from the burner 48 may be passed through line 52 into down flow leg or standpipe 26 of **U**-bend 24.

Steam may be introduced into riser 22 above constriction 32 and at line 54 if desired. The amount of stream introduced through line 28 controls the rate of circulation of solids through **U**-bend 24 as above described.

The oil feed is preheated in any suitable manner to a temperature preferably between about 500° and 750° F. before being introduced into the reactor 10. The preheating of the heavy oil is done to reduce the viscosity of the oil feed and render it fluid and also to reduce the heat load in the reactor. The oil feed comprises a residual petroleum oil such as tar, pitch, crude residuum, heavy bottoms or other similar hydrocarbon stock having an API gravity between about −10 and 20°, a Conradson carbon between about 5 and 50 wt. % and an initial boiling point between about 850° and 1200° F. Some steam may be added with the oil feed in line 18 if desired.

The fluidized bed 12 is maintained as such by the upflowing hydrocarbon gases and vapors formed by the coking of the oil feed and by the steam added through line 28 to riser 22. The superficial velocity of the gases and vapors passing upwardly through the bed 12 is between about 0.5 and 5 feet per second when using finely divided coke of about 50 to 400 microns the density of the fluidized bed will be about 40 pounds per cu. ft., but may vary between about 30 and 60 pounds per cu. ft. depending on the gas velocity and particular particle size range selected.

Vaporous products of coking leave bed 12 and pass overhead through cyclone separator arranged in the top interior of the reactor 10. The vaporous products contain entrained solids and the separator 56 is used to separate or recover entrained solids and return them through dip leg 58 to dense fluidized bed 12. The separated vapors pass overhead from separator 56 through line 60 for further treatment as by fractionation or condensation to recover desired products.

Standpipe 26 is provided with one or more aerating or fluidizing lines 62. The bottom of **U**-bend 24 may be aerated by introducing gas through one or more lines 64.

Returning now to the reactor 10, coke or coked particles are withdrawn from the dense bed as a dense fluidized mixture through line 66 and preferably passed through stripper diagrammatically shown at 68 to remove volatile hydrocarbons therefrom. Stripping gas from the stripper is returned to the reactor.

When more coke is being produced than is necessary to supply heat to the reactor, it can be withdrawn as product coke from line 70 through line 72.

Coke particles from line 70 which are to be burned in the burner diagrammatically shown at 48 are mixed with air or other oxygen-containing gas introduced through line 74, preferably at the inlet of burner 48 which may be of a low velocity dense fluidized bed burner or a high velocity transfer line burner to burn coke and raise the temperature of the coke particles to a temperature about 50 to 600° F. higher than that of the particles in the dense bed 12 in the coking zone. The temperature in the burner may be between about 1100° F. and 1600° F. The hot coke particles from burner 48 are passed through line 49 in any suitable manner and some of the hot coke particles are returned through line 78 to the bottom portion of dense bed 12 in the coking zone. The rest of the hot coke particles from line 49 are passed through lines 50 and 52 to **U**-bend 24 as above described.

During combustion of the coke or other coke-containing particles in burner 48, the particles are heated to a temperature higher than that in reactor 10 so that when the particles are recirculated to the reactor 10 they will contain sufficient heat to supply the heat of vaporization and

cracking of the oil feed introduced into riser 22 and dense bed 12.

The fluidizing gas and solids from riser 22 may be distributed at the bottom of the reactor 10 either by conventional perforated grid, a packed conical section or a number of open conical inlets. The distribution grid or the like may be omitted, if desired.

Referring now to Fig. 3 the same reference characters are used for designating the parts as in Fig. 1. Certain parts have been omitted from Fig. 3 but this has been done merely to simplify the description. In this modification an internal recycle means is used which comprises a vertical draft tube 82. Draft tube 82 is an open ended pipe aranged vertically with its bottom end 84 spaced above the bottom 25 of reactor 10 and with its upper end 86 below dense bed level 14 so that the tube 82 is submerged in the dense bed 12.

As shown in the drawing residual oil feed is passed through line 88 and introduced into an intermediate portion of draft tube 82 through one or more nozzles 90 preferably discharging upwardly into tube 82 in the direction of flow of solids through tube 82. Aerating gas such as superheated steam is introduced into tube 82 below the locus of introduction of oil feed. The steam is passed through line 92 and injected into tube 82 through one or more nozzles 94. A high rate of solids circulates from the conical bottom 25 of reactor 10 up through draft tube 82 past the steam injection point 94 and the oil feed nozzles 90.

In the preferred form of draft tube the oil feed is injected into a constricted zone such as a Venturi section as described above in connection with Fig. 1 in riser 22 at 32. As described in connection with riser 22 in Fig. 1, the residual oil may be introduced at a plurality of regions into draft tube 82 in a similar manner. Also if desired more refractory stock may be introduced into tube 82 at a region below that of the introduction of the residual oil feed. The diameter of the draft tube may be varied between about $^1/_5$ to $^1/_2$ the diameter of the reactor. When the draft tube is relatively narrow, more gas may be added to result in a higher velocity in the draft tube without exceeding the desired velocities of 3 to 5 ft. per second at the interface 14.

In a specific example about 100 barrels per day of residual hydrocarbon oil having an API gravity of 10°, a Conradson carbon of 18 and an initial boiling point of about 1150° F. is introduced into riser 22 through line 18. The oil is preheated to about 600° F. The temperature in riser 22 and dense bed 12 is 1000° F. and in the burner 48 is 1150° F. About 5 wt. % of steam on the oil fed through line 18 is introduced into riser 22 through line 28 below the constriction 32. The amount of steam introduced through line 28 may be varied between about 2 and 5 wt. % on the oil feed.

The riser 22 may be between about 10 and 50 feet in length, the longer sizes being preferred to allow time for some cracking to occur in the riser and thus provide more gas in the riser for aeration of the fluid bed 12 and to reduce reactor solids hold up. When using one riser 22 and a circulation of 10000 lbs to 25000 lbs. of coke per hour riser 22 has a diameter between about 0.3 and 0.4 feet and the constriction 32 at its "vena contracta" is between about 0.1 and 0.2 feet. The reactor 10 is between about 1 and 2 feet in diameter and between 10 and 30 feet in height.

In the above example all the hot coke particles from burner 48 were introduced into dense bed 12 from line 78.

For a similar size design for the modification shown in Fig. 3 and the same size reactor, the draft tube will be between about 5 and 15 feet in length and between 0.3 and 1 feet in diameter and arranged between about 1 and 5 feet above the bottom 25 of vessel or reactor 10.

The circulating solid in the above example is coke having a particle size between about 35 and 100 standard mesh with the majority of the particles being between about 48 and 80 mesh. The superficial velocity of the gas in the reactor 10 was about 1 ft. per second at the bottom and the density of the fluid bed 12 was about 40 lbs. per cubic foot. The superficial gas velocity in constriction 32 was about 50 feet per second and the solids to gas ratio passing through the constriction 32 is about 10 lbs. per cubic foot.

The overhead products from line 60 were quenched to a temperature of about 800° F.

The yields obtained from the above example were as follows:—

C_3—wt. %	6.5
C_4—vol. %	2.8
C_5—430° F. vol. %	15.0
430—650° F. vol. %	10.7
650—1050° F. vol. %	30.0
1050° F.+vol. %	30.0
Coke wt. %	10.0

About 145 lbs. of coke per hour are withdrawn as product coke through line 72.

If it is desired to raise the temperature of the solids in standpipe 26 or riser 22 or to maintain a desired temperature therein, hot particles from burner 48 may be passed through line 52 and/or 50.

This invention is capable of feeding residua or residual oils which contain large amounts of solids such as coke or sediment which would plug the conventional spray type nozzle. Larger amounts of slurry oil containing solids may be returned to the unit to compensate for loss of coke fines from the coking unit.

What we claim is:—

1. A method of converting into lower-boiling hydrocarbons heavy hydrocarbon oils which consist of constituents which cannot be vaporized without cracking at atmospheric pressures, which comprises introducing preheated heavy hydrocarbon oil in a mixing zone while passing through said mixing zone solid non-catalytic refractory particles at a turbulent velocity, passing the resultant mixture of oil and solid particles into a dense fluidized bed of similar solid refractory particles maintained in a reaction zone at an elevated temperature to produce lower boiling hydrocarbons therein while depositing coke on the said solid particles, removing the coked solid particles from the said reaction zone and passing them to a combustion zone wherein oxygen-containing gas is introduced to burn the coke and heat the solid particles to a temperature above that existing in the said reaction zone, returning at least part of the heated particles from the said combustion zone to the said dense fluidized bed to supply heat thereto.

2. A method as claimed in Claim 1 which is a method of coking residual oils.

3. A method as claimed in Claim 1 or Claim 2 wherein the said solid refractory particles are coke particles.

4. A method as claimed in any of Claims 1 to 3 wherein the said mixing zone comprises a **U**-shaped passageway situated externally to the said reaction zone, one leg of the said **U**-shaped passageway extending downwardly from the said dense fluidized bed of solid refractory particles, and the other leg extending upwardly into the bottom of the said reaction zone, whereby solid fluidized particles are withdrawn from the said dense bed, and pass through the **U**-shaped passageway at a turbulent velocity, and preheated heavy oil feed is introduced into the turbulent stream of solid particles therein at a point on the upflow leg of the said **U**-shaped passageway, and wherein the turbulent velocity of the solid particles and/or mixture thereof in the said **U**-shaped passageway is maintained by the introduction of aerating gas at one or more points therein.

5. A method as claimed in Claim 4 wherein the **U**-shaped passageway is restricted in diameter in the region of the point or points of entry of the said preheated heavy oil.

6. A method as claimed in Claim 4 or Claim 5 wherein the upflow leg of the said **U**-shaped passageway is of sufficient length to permit therein some conversion of the heavy oil to lower-boiling hydrocarbons.

7. A method as claimed in any of Claims 4 to 6 wherein at least a part of the hot decoked refractory solid particles from the combustion zone are passed to within the downflow leg of the said **U**-shaped passageway.

8. A method as claimed in any of Claims 4 to 7 wherein at least a part of the hot decoked refractory solid particles are passed to within the upflow leg of the said **U**-shaped passageway.

9. A method as claimed in any of Claims 1 to 3 wherein the said mixing zone comprises a vertical draft tube submerged in the said fluidized bed of solid refractory particles, whereby solid refractory particles pass through the said draft tube at a turbulent velocity, the said turbulent velocity being maintained by the introduction of aerating gas into the said draft tube, and preheated heavy oil feed is injected into the turbulent flow of refractory particles at one or more intermediate points in the said draft tube, and the mixture of refractory solids and heavy oil passes therefrom into the said fluidized bed.

10. A method as claimed in Claim 9, wherein the said draft tube is restricted in diameter at the point or points of entry therein of the said preheated heavy oil.

11. A method as claimed in Claim 9 or Claim 10, wherein hot decoked refractor solid particles from the combustion zone are passed to the said draft tube.

12. A method as claimed in any of Claims 4 to 11, wherein the said aerating gas is superheated steam.

13. Improved methods of converting into lower-boiling hydrocarbons heavy hydrocarbon oils as hereinbefore described and illustrated in the accompanying drawings.

14. The apparatus for carrying out the methods as claimed in any of the above claims.

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754,966 COMPLETE SPECIFICATION
1 SHEET
This drawing is a reproduction of the Original on a reduced scale.

FIG. 1.

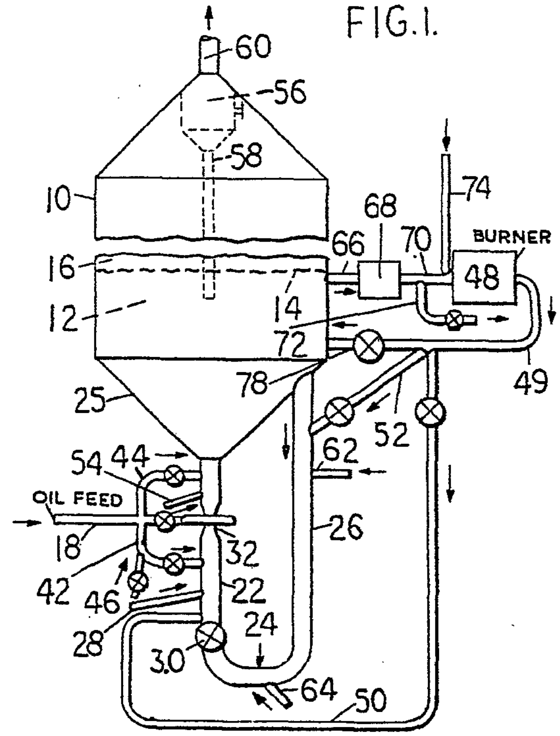

FIG. 2.

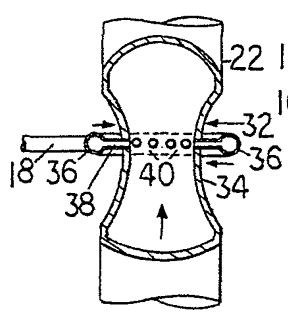

FIG. 3.